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Unique Radioanalytical Protocols for Characterization and Verification during Decontamination and Decommissioning

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ABSTRACT

In order to successfully decontaminate, deactivate and decommission surplus Department of Energy (DOE) facilities throughout the Savannah River Site (SRS), a variety of characterizations must be completed to sufficiently identify and quantify potential contaminants of concern. The ultimate goal is to *rapidly and efficiently* characterize, decontaminate (if necessary), and verify that the remnants meet specified limits established by either an industrial worker model or a groundwater model. To meet this end, the Savannah River National Laboratory (SRNL) developed a series of radioanalytical strategies and methodologies which can be used to characterize targeted facilities and prove that decontamination has been sufficient.

To our knowledge, this is the first application of this novel methodology within the DOE complex. This methodology has been successfully utilized with nearly 1000 samples from over a dozen facilities. The application of this approach to just a single facility shortened the schedule by 30 days and resulted in non-labor dollar savings of over $60K. Cost savings for a second facility was determined to be $375K. Based on the success of this methodology at SRS, this approach will be valuable to other nuclear facilities in the USA and abroad involved with the decontamination and decommissioning process.

INTRODUCTION

In recent years, a large degree of focus has been placed on the decontamination, deactivation, and decommissioning of inactive facilities throughout the Savannah River Site Nuclear Complex. The process of decommissioning facilities involves removal actions which are supported throughout numerous stages by radiological characterization of the material slated for removal, and confirmatory analyses of material which is to be left in place. The process is generally tied to very aggressive schedules.

The Savannah River National Laboratory (SRNL) can rigorously quantify the possible radiological contaminants of concern (COCs) encountered in Site facilities utilizing radiochemical separations and analyses; however, these analyses can be costly and time-consuming. Therefore, it was necessary to develop a faster, cheaper, accurate, and technically defensible approach for the analysis of concrete powder samples with wide ranges of contamination levels and varying constituents. In response to this challenge, a “bounding” approach was designed to characterize the samples to a level at or below the level defined by the acceptable risk-thus proving that the facility of interest has been fully characterized and successfully decontaminated.

The utilization of this approach employs a unique process in which:

- a list of radionuclides requiring evaluation is optimized,
- the Derived Concentration Guideline Levels (DCGLs) in an SRNL Technical Guidance Document are utilized to determine target detection levels for the radionuclides requiring evaluation,
- a staged analysis approach is developed to quantify the radionuclides to the target detection levels, and
- necessary analyses are carried out to sufficiently provide empirical data in a time-and cost-efficient manner.

This paper will provide in-depth details on the successful application of this “bounding” approach.

OPTIMIZATION OF RADIONUCLIDES TO BE QUANTIFIED

At the onset of work for a given facility, Site Deactivation and Decommissioning (SDD) and SRNL personnel generate a list of contaminants of concern (COCs) for the facility. This requires knowledge of the facility’s historical missions and details of the processes utilized to accomplish those missions (i.e., process knowledge). Some facilities had limited missions and highly controlled processes, so the associated process knowledge is well defined and easily obtained. However, some facilities had missions dating to the 1950s, and/or missions that changed many times throughout the life of the facility. In these instances, process knowledge alone is not complete enough to formulate a rigorous understanding of possible COCs.

Regardless of the extent of available process knowledge, it serves as the starting point to generate an initial list of COCs. Sampling evolutions from areas which are known to be or are most likely to be contaminated (spill areas, secondary containments, sumps, pits, and the like) are then performed. Samples from these evolutions are exhaustively analyzed for a complete spectrum of potential isotopes. The resultant analytical data, coupled with the process knowledge, are used to finalize the list of COCs. Table I provides an example of a COC list utilized for a recent facility.

Table I. Example of a Typical List of Contaminants of Concern

Tritium	I-129	U-238
C-14	Cs-137	Pu-238
Ni-59	U-233	Pu-239
Co-60	U-234	Pu-240
Ni-63	U-235	Am-241
Sr-90	U-236	Pu-242
Tc-99	Np-237	Cm-242

DETERMINATION OF TARGET DETECTION LEVELS

Nuclides on this list of COCs are required to be quantified in concrete which has been statistically sampled from the facility. The quantification process is used to prove that the maximum allowable contamination at the Savannah River Site (SRS) has not been exceeded. For the SRS, detection levels for radionuclides included on the list of COCs are determined using Derived Concentration Guideline Levels (DCGLs) from SRS Technical Guidance Document WSRC-TR-2003-00448. This Technical Guidance Document utilizes risk modeling for both the industrial worker and impact to groundwater as required by the contract specific clean-up criteria. It reports both radionuclide-specific Industrial Worker DCGLs determined using RESRAD (Residual Radioactivity) to identify the 1.0E-04 risk to the industrial worker and area specific Groundwater Impact DCGLs determined using VZCOMML (Vadose Zone Contamination Model Multi-Layer) to identify contaminants likely to pose a threat to groundwater in 1000 years. In simplistic terms, the process involves a limit that is associated with risk. Quantified risk below the limit is acceptable, quantified risk above the limit is not acceptable.

Table II illustrates the radionuclides to be quantified per Table I and the level to which the quantification is required based on the DCGLs. The target detection levels utilized for analysis planning are the most restrictive of the following two limits: area specific groundwater impact DCGLs derived from VZCOMML or 10% of the 1E-04 industrial worker risk derived from RESRAD. The 10% is a result of industrial risk values being cumulative; the sum of the DCGL/actual result must be less than 1; or the total can not be greater than 100%. The groundwater limit is not cumulative; if radionuclides are quantified below the limit they meet the criteria for acceptable risk. Any radionuclide quantified above the groundwater limit does not meet the criteria for acceptable risk, or fails.

Table II. Example of Radionuclides to be Quantified and Their Target Detection Levels

Radionuclide	**Target Detection Levels 0.1x1E-04 Risk Industrial Worker DCGL (pCi/g)**	**Target Detection Levels Area VZCOMML Groundwater DCGL (pCi/g)**
H-3	6.94E+07	6.41E+03
C-14	1.90E+07	
Ni-59	3.73E+06	
Ni-63	1.65E+06	
Co-60	1.12E+00	
Sr-90	4.31E+03	
Y-90	4.31E+03	
Tc-99	7.18E+05	8.65E+02
I-129	4.17E+03	9.60E-01
Cs-137	3.18E+00	
U-233	9.74E+02	
U-234	2.83E+03	
U-235	5.35E+00	
U-236	3.54E+03	
U-238	3.02E+01	
Np-237	4.03E+00	
Pu-238	1.62E+03	
Pu-239	1.38E+03	
Pu-240	1.46E+03	
Pu-242	1.55E+03	
Am-241	7.58E+01	
Cm-242	3.31E+03	

DEVELOPMENT OF ANALYSIS STRATEGY

Once the target detection levels are determined, a series of analyses are designed to meet the target detection levels for all of the nuclides in Table II. Often, many of the target detection levels are quite low, so rigorous radiochemical separations and analyses are required to sufficiently quantify these particular nuclides. However, many of the target detection levels are often high enough to negate the need for rigorous separations and analyses. In these cases, gross analyses are utilized to provide initial quantification. If the gross results are below the target detection limits, no further analyses are required. If the gross results are above the target detection limits, further analyses are selectively targeted based upon the gross results.

In short, a combination of nuclide-specific analyses coupled with gross analyses can be utilized to support SDD customers throughout many stages of their work to determine whether acceptable risk levels have been met. These analyses are carried out in a staged approach, which is clarified in the following sections. The COCs and target detection levels listed in Table II will be used as the skeleton of the outline. It should be noted that each stage of analyses is customized for the specific facility undergoing the D&D process, which carries with it unique COCs and DCGLs. The details are customized to meet the requirements of each specific facility; however, the overall process is similar for all facilities at SRS.

STAGE 1 ANALYSES

Initially, concrete samples submitted to Savannah River National Laboratory in support of this type of work are analyzed using a combination of the following methods: tritium distillation followed by liquid scintillation analysis, I-129 separation followed by low energy gamma pulse height analysis, gamma pulse height analysis using high purity germanium detectors, Ni-59 via low energy gamma pulse height analysis, gross alpha analysis, gross nonvolatile beta analysis, and gross total beta analysis. These seven analyses are utilized for the COCs in Table II as illustrated in Table III.

Table III. Stage 1 Analyses in Support of Table II Radionuclides

Radionuclide	**Source**
Tritium	Tritium Separation and Analysis
C-14	Gross Total Beta Analysis
Ni-59	Ni-59 via Gamma Pulse Height Analysis
Co-60	Gamma Pulse Height Analysis
Ni-63	Gross Total Beta Analysis
Sr-90	Gross Nonvolatile Beta Analysis
Tc-99	Gross Total Beta Analysis
I-129	I-129 Separation and Analysis
Cs-137	Gamma Pulse Height Analysis
U-233	Gross Alpha Analysis
U-234	Gross Alpha Analysis
U-235	Gamma Pulse Height Analysis
U-236	Gross Alpha Analysis
Np-237	Gamma Pulse Height Analysis
U-238	Gross Alpha Analysis
Pu-238	Gross Alpha Analysis
Pu-239	Gross Alpha Analysis
Pu-240	Gross Alpha Analysis
Am-241	Gamma Pulse Height Analysis
Pu-242	Gross Alpha Analysis
Cm-242	Gross Alpha Analysis

Specific information pertaining to the application of each method to the characterization of concrete samples follows.

Tritium

The tritium analysis involves a separation via distillation followed by liquid scintillation analysis. The DCGL-based target detection level from Table II is utilized to plan the analysis and the associated analysis detection limit. The relatively low target detection level in Table II necessitates the rigorous radiochemical separation and analysis for this nuclide.

I-129 Separation and Analysis

The low energy of the I-129 gamma emission, in addition to the low targeted detection level required by this example, necessitates a rigorous radiochemical separation and analysis for this nuclide. The I-129 separation and analysis involves a silver iodide precipitation followed by low energy gamma analysis. Neutron activation analysis is used to yield the separation.

Gamma Pulse Height Analysis

The gamma pulse height analysis using an n-type high purity germanium detector provides the ability to quantify: Co-60, Cs-137, U-235, Np-237, Am-241, Am-243 via the Np-239 daughter, Cm-243, Cm-244, U-235, U-238 if low detection limits are not needed, Ac-228, Sb-124, Sb-125, Ba-133, Bi-212, Bi-214, Cf-249, Cf-251, Ce-141, Ce-144, Cs-134, Cs-137, Co-57, Co-58, Co-60, Eu-152, Eu-154, Eu-155, Pb-212, Mn-54, Np-239, Nb-94, K-40, Pm-144, Pm-146, Ru-103, Ru-106, Na-22, Tl-208, Sn-113, Sn-116, Y-88, Y-90, Zn-65, and Zr-95.

This is not an exhaustive list, and there are many other ways to quantify some of these listed isotopes. The DCGL-based target detection levels from Table II are utilized to plan the analysis and the associated method detection limit. All observed nuclides deemed to be present above the lower level of detection are reported. Results below the lower limit of detection are not reported for isotopes unless they are listed as COCs.

Ni-59 Analysis

Ni-59, which undergoes electron capture, is detectable via low energy gamma pulse height analysis. The DCGL-based target detection level from Table II is utilized to plan the analysis and the associated method detection limit. Due to the large magnitude of the target detection limit in this example, no radiochemical separation was deemed necessary for this nuclide prior to low energy gamma pulse height analysis. Bypassing the unnecessary radiochemical separation, when possible, increases the efficiency of the characterization analyses.

Gross Alpha Analysis

The gross alpha analysis provides total, non-speciated alpha activity-it is not isotope specific. This total alpha activity can be used to provide an upper limit for the following alpha-emitting nuclides in this example: U-233, U-234, U-236, U-238, Pu-238, Pu-239, Pu-240, Pu242, and Cm-242. For this example, the DCGL-based target detection level for U-238 would be utilized to plan the analysis and the associated method detection limit, since it is the most restrictive of the listed alpha-emitting nuclides. The total reported alpha activity represents the maximum level for the combination of all the isotopes listed in this paragraph. If the reported gross alpha measurement is above the target detection level for any of the listed alpha-emitting nuclides, further Stage 2 analyses would be carried out as described later in this paper. No further analyses would be required for any of the isotopes for which the reported gross alpha measurement is below the target detection level. Bypassing any unnecessary radiochemical separations increases the efficiency of the characterization analyses.

Gross Total Beta Analysis

The gross total beta analysis provides total, non-speciated beta activity-it is not isotope specific. This total beta activity is used to provide an upper limit for the following beta-emitting nuclides in this example: C-14, Ni-63, and Tc-99. For this example, the DCGL-based target detection level for Tc-99 would be utilized to plan the analysis and the associated method detection limit, since it is the most restrictive of the listed beta-emitting nuclides. The total beta activity represents the maximum level for the combination of all the isotopes listed in this paragraph. If the reported gross total beta measurement is above the target detection level for any of the listed beta-emitting nuclides, further Stage 2 analyses would be carried out as described later in this paper. No further analyses would be required for any of the isotopes for which the reported gross total beta measurement is below the target detection level. Bypassing any unnecessary radiochemical separations increases the efficiency of the characterization analyses.

Gross Nonvolatile Beta Analysis

The gross nonvolatile beta analysis provides total, non-speciated beta activity- it is not isotope specific. This total nonvolatile beta activity is used to provide an upper limit for the following beta-emitting nuclides in this example: Sr-90 and Y-90. The DCGL-based target detection levels from Table II are utilized to plan the analysis and the associated method detection limit. For this example, the target detection levels for Sr-90 and Y-90 were much lower than those for the other beta-emitting nuclides, so some pretreatment would be required to concentrate the sample matrix. This pretreatment would remove volatile beta constituents. This volatilization, coupled with the target detection levels, provides the justification for analyzing for both total beta activity and nonvolatile beta activity. The total nonvolatile beta activity represents the maximum level for the combination of all the isotopes listed in this paragraph. If the reported gross nonvolatile beta measurement is above the target detection level for Sr-90 or Y-90, further Stage 2 analyses would be carried out as described later in this paper. Bypassing the unnecessary radiochemical separation, when possible, increases the efficiency of the characterization analyses.

STAGE 2 ANALYSES

If the Stage 1 results for all applicable COCs are proven to be below the risk-related target detection levels, no further analyses are required. However, if a nuclide is quantified via a gross method, and the gross result is above the target detection level, follow-up is required utilizing the more rigorous radiochemical separation and analysis. The rigorous radiochemical separations and analyses are performed only when necessary; consequently, the overall analysis cost is reduced and the schedule is accelerated.

Provided the activity levels in the samples are low enough, the Stage 1 analyses can successfully complete the entire characterization outlined in Table II. Stage 2 analyses are utilized, as previously mentioned, in cases in which the gross analyses provide results above the targeted detection levels. When a gross result is above the target detection level for any specific nuclide, a more rigorous radiochemical separation and analysis is carried out for that nuclide. This is accomplished using any number of the following methods: Tc-99 separation and analysis, C-14 separation and analysis, Ni-59/Ni-63 separation and analysis, Sr-90 separation and analysis, ICP-MS, plutonium separation and analysis, or americium/curium separation and analysis. These radiochemical separations, which are complex and time-consuming, utilize a large portion of the laboratory's resources. Bypassing these involved methods, when possible, greatly increases the efficiency and economy of the characterization analyses without negatively impacting the data quality provided for the SDD customer.

CONCLUSIONS

This staged approach enables technically defensible rapid characterization of a large number of samples in a relatively short amount of time. It has been successfully utilized to determine whether risk criteria have been met with nearly 1000 samples from over a dozen facilities. The application of this approach to just a single facility shortened the schedule by 30 days and resulted in non-labor dollar savings of over $60K. Cost savings for a second facility was determined to be $375K. Based on the success of this methodology at SRS, this approach will be valuable to other nuclear facilities in the USA and abroad involved with the decontamination and decommissioning process.